

Energy loss of atoms at metal surfaces due to electron-hole pair excitations: First-principles theory of ‘chemicurrents’

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A method is presented for calculating electron-hole pair excitation due to an incident atom or molecule interacting with a metal surface. Energy loss is described using an *ab initio* approach that obtains a position-dependent friction coefficient for an adsorbate moving near a metal surface from a total energy pseudopotential calculation. A semi-classical forced oscillator model is constructed, using the same friction coefficient description of the energy loss, to describe excitation of the electron gas due to the incident molecule. This approach is applied to H and D atoms incident on a Cu(111) surface, and we obtain theoretical estimates of the ‘chemicurrents’ measured by Nienhaus et al [Phys. Rev. Lett. **82**, 446 (1999)] for these atoms incident on the surface of a Schottky diode.

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Considerable progress has been made in recent years in the theory of gas-surface interactions. This has been due to the parallel developments of large-scale electronic structure calculations based on density functional theory, combined with multi-dimensional quantum and classical analysis of the dynamics [1, 2]. Despite these advances there remains one key area that is still largely unexplored and poorly understood; the process of energy dissipation into substrate degrees of freedom. Although this is known to be of central importance in many situations [2], there exist few ‘real’ calculations to date for the energy loss to either phonons or electrons in the surface [3].

In particular there have been a number of recent experiments that provide convincing evidence that energy dissipation by the creation of electron-hole (*e-h*) pairs is a significant effect in gas-surface dynamics [4, 5]. Of particular interest for this Letter are the results of Nienhaus and co-workers [6, 7] who directly measured the hot electrons and holes created at Ag and Cu surfaces by the adsorption of thermal hydrogen and deuterium atoms in the form of a ‘chemicurrent’ in a Schottky diode. Here we report *ab initio* calculations of *e-h* pair creation for H/Cu(111) and the resulting chemicurrents.

The calculation proceeds in three stages. First, a standard Kohn-Sham (KS) total energy calculation is carried out for a range of positions of the incident atom. Second, the resulting KS states and potentials are used to obtain a friction coefficient for the motion of the atom via Time Dependent Density Functional Theory (TDDFT). Finally, a classical trajectory for the incident atom is calculated and a forced oscillator model (FOM) is used to obtain a semi-classical (classical atomic motion coupled to quantum metallic electrons) description of *e-h* pair

creation. It is important to note that our theory refers to a nearly adiabatic process with multiple low energy excitations. This is in contrast to the truly nonadiabatic charge transfer models used to describe, for example, exoemission of electrons [8].

The initial total energy calculation provides the ground state properties of an interacting surface/atom system using a plane-wave basis, pseudopotentials and a super-cell geometry. This super-cell method has the advantage that it retains the continuous spectrum of one-electron excitations, unlike cluster models [9], which is important for the interactions considered here. The resulting KS eigenstates are used to evaluate the friction coefficient, η , associated with the motion of an atom at a chosen position and in a direction of choice, $\hat{\mathbf{h}}$, using the method described in a previous paper [10]. This applies TDDFT together with a quasi-static limit [11], and in essence consists of the evaluation of the expression

$$\eta = 2\pi\hbar \sum_{\alpha, \alpha'} \left| \langle \epsilon_{\text{F}} \alpha | \hat{\mathbf{h}} \cdot \nabla V | \epsilon_{\text{F}} \alpha' \rangle \right|^2 \quad (1)$$

where α are supplementary quantum numbers for states on the Fermi surface, and $\hat{\mathbf{h}} \cdot \nabla V$ is the rate of change of the self-consistent KS potential with atomic position. As described in [10], care must be taken to interpret the super-cell geometry correctly when evaluating Eq. (1) within a plane-wave basis, since the system of interest consists of the isolated motion of an atom at a surface, while the super-cell naturally describes a coherent lattice in motion. It is also important to perform a correct discretisation of Eq. (1) within the finite available sampling of \mathbf{k} space [10].

These first two steps provide the total energy and fric-

tion coefficient at positions of choice and thus it is possible to obtain the classical trajectory of an atom near the surface. This provides the classical dynamics of the interaction such as the total energy loss and the critical initial kinetic energy, ϵ_c , defined as the initial energy below which the atom is trapped in the surface well. For simplicity, only the case of a single atom incident perpendicular to the surface is considered here, and this trajectory is denoted by $z(t)$.

Electron-hole pair excitations can be further analysed by implementing a FOM [2] description of the energy loss to the electron gas. This provides a straightforward, if approximate, quantum calculation of the response of the electron gas to the time varying self-consistent potential resulting from the classical motion of the incident atom. Past work [12, 13, 14] has shown that the probability density that an incident atom will excite an e - h pair of energy $\hbar\omega$, given that a single e - h excitation event has occurred, can be written as

$$\frac{P_s(\omega)}{\alpha_0} = \frac{1}{\alpha_0} \frac{1}{\omega} \sum_{\alpha, \alpha'} \left| \int_{-\infty}^{\infty} \langle \epsilon_F \alpha | \hat{\mathbf{h}} \cdot \nabla V | \epsilon_F \alpha' \rangle \dot{z}(t) e^{-i\omega t} dt \right|^2, \quad (2)$$

where $\alpha_0 = \int_{-\infty}^{\infty} P_s(\omega) d\omega$ is the total number of e - h pairs created by multi-excitation events. Eq. (2) uses the ‘Boson Approximation II’ described by Schönhammer and Gunnarsson [12, 15]. This approximation is constructed by using adiabatic electronic states in place of the true states and assuming that the matrix elements vary sufficiently slowly with energy that they can be approximated by the values taken at the Fermi energy. All information about the system and its evolution is contained in $P_s(\omega)$, together with the assumption that individual e - h excitation events are uncorrelated. The probability that an incident atom will excite n e - h pairs is then given by $e^{-\alpha_0} \alpha_0^n / n!$. This allows a multi-excitation expansion to be used to obtain the total energy loss of the incident atom, although this is not necessary for our purposes [12].

Although Eq. (2) may be evaluated by the same approach used to obtain the friction coefficient, this requires the storage and interpolation of a large number of matrix elements. Due to the approximations already made to develop the theory to this point this effort does not seem justifiable. Instead, we assume that the dependence of the matrix elements in Eq. (2) on z and α, α' can be expressed in the separable form $f_{\alpha, \alpha'} g(z)$. Physically, this implies that each e - h pair excitation experiences the same time-dependent force, but with different strengths. This leads to

$$P_s(\omega) = \sum_{\sigma} \frac{1}{\pi \hbar \omega} \left| \int_{-\infty}^{\infty} \eta_{\sigma}^{\frac{1}{2}}(z) \dot{z}(t) e^{-i\omega t} dt \right|^2 \quad (3)$$

where different spin terms are shown explicitly (subscript σ). The same approach has been used by previous authors [2, 14, 15, 16], and it can be shown that the mean

excitation energy of the electron gas (at any instant) is the same for $P_s(\omega)$ in Eqs. (2) and (3).

The FOM may be used to calculate various physically measurable quantities, such as the sticking probability and average energy loss of the incident atom. Here we are interested in the number of electrons excited above a given energy $\epsilon_s = \hbar\omega_s$ (relative to the Fermi energy) as a result of the multiple e - h excitations. This quantity is given by

$$N_e(\omega > \omega_s) = \int_{\omega_s}^{\infty} d\omega \int_{\omega}^{\infty} d\omega' \frac{P_s(\omega')}{\omega'}, \quad (4)$$

and is of particular interest because it provides a direct estimate of the number of electrons made available for detection as a ‘chemicurrent’ in the experiments described by Nienhaus *et al.* [6].

We also note that Eq. (3) does not take into account any loss of coherence due to the finite lifetime of excited electrons. Preliminary estimates of this effect show that a finite lifetime is important for heavy (i.e. slow moving) adsorbates, but for the systems considered here the chemicurrent changes by at most 40% [17].

H/Cu(111) and D/Cu(111) Calculations of the interaction energy, friction coefficient, dynamics and e - h pair creation have been carried out for both H and D atoms moving perpendicular to the surface above the top site of Cu(111). This system has been chosen for simplicity (although it should be noted that spin polarisation is needed to obtain the correct behaviour for large atom-surface separations) and because of its relevance to the ‘chemicurrent’ experiments of Nienhaus *et al.* [6]. Calculations have also been carried out for H/D above the hcp hollow site, and for motion parallel to the surface - hcp results are similar to those for the top site in terms of e - h pair creation, so here we report only the latter. Full results will be presented elsewhere [17].

The surface is modelled by a five-layer slab, with a vacuum gap equivalent to another five layers. A 2×2 in-plane super-cell is used - tests show that the deformation potential ($\hat{\mathbf{h}} \cdot \nabla V$) caused by the displacement of H atoms is well localised within this unit cell. A spin-polarised version of the PW91 functional is used for exchange-correlation effects (see [18], and references therein), a Troullier-Martins [19] pseudopotential is used for Cu, and H is represented by a Coulomb potential. The plane-wave, pseudopotential code CASTEP is used to obtain the self-consistent potentials and KS states. Calculations are performed with a plane-wave cut-off of 830 eV, 54 k-points are included in the full surface Brillouin zone, and a Fermi surface broadening of 0.25 eV is used. Total energy calculations are performed for a range of heights between 1.0 and 4.0 Å above the surface.

Friction coefficients are evaluated for the same range of heights and for motion perpendicular to the surface, as described by Trail *et al.* [10]. The natural way to do calculations of this type is to assume spin-adiabaticity

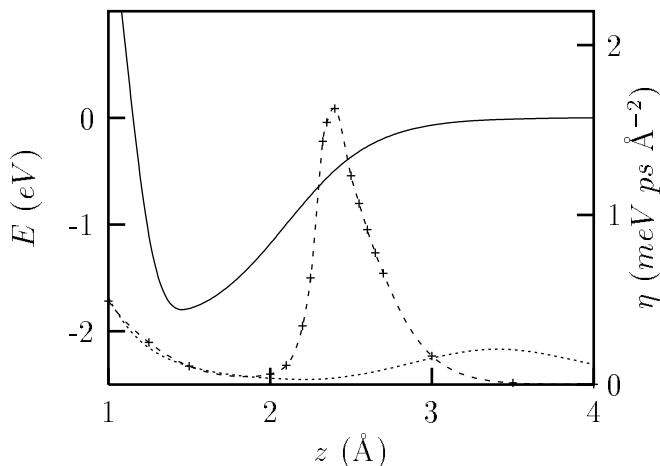


FIG. 1: Potential energy (solid line) and friction coefficient for H atom in perpendicular motion above the top site of Cu(111). Dashed line is friction resulting from constrained spin calculations, and dotted line for the spin degenerate case.

and minimise the total energy of the system with respect to the magnetisation density, as well as the charge density. Surprisingly, this leads to unphysical results. As the atom approaches the surface a phase transition from spin polarised to spin-degenerate occurs, as the H affinity level crosses the Fermi level [17, 20], and $\hat{\mathbf{h}} \cdot \nabla V_{xc}$ becomes singular at this point. This results in a z^{-1} singularity in η and it is straightforward to show that this divergence leads to infinite stopping power, i.e. incident particles of any energy are stopped at the singular height. Numerical calculations confirm the existence of the singularity at a height of 2.39 Å above the surface [17].

We take our assumption of spin-adiabaticity to be the source of this unrealistic behaviour. An alternative approach is to assume that the period of time that the atom spends near the critical height is not large enough for spin relaxation to occur, leading to a formulation where the net polarisation of the system is held fixed at its initial value.

Figure 1 shows the resulting potential energy curve and friction coefficient for the constrained spin calculations. This friction differs significantly from the fully spin relaxed friction for $2 < z < 3$ Å; a peak is still present as the affinity level crosses the Fermi energy, but it is no longer singular. The friction coefficient for a spin-degenerate calculation (expected to be inaccurate for z above the critical height) is also shown for comparison. In the remainder of this paper constrained spin data are used for all results unless explicitly stated otherwise, but a comparison of constrained with degenerate spin will allow us to assess the significance of the friction in different regions of space to our final results.

A standard Verlet integration is carried out to obtain the classical trajectories for an incident H or D atom,

based on the data of Fig. 1 and for a range of initial kinetic energies. The classical trajectories show expected features, with a critical initial kinetic energy of $\epsilon_c = 166$ (115) meV for H (D), and an escaping atom spending ~ 0.04 ps in the potential well [$z(t) < 3.0$ Å].

We now turn to the number of electrons excited above a given energy ϵ_s (relative to the Fermi energy), $N_e(\epsilon > \epsilon_s)$. For a Schottky barrier of 0.6-0.65 eV, and a thermal flux of H atoms (300 - 350K) perpendicularly incident on the clean Cu surface of a Cu/Si Schottky diode at 135K, Nienhaus *et al.* [6] detected 1.5×10^{-4} electrons/atom.

Equation (4) is applied to the results of the FOM calculations, with $\epsilon_i = \frac{3}{2}kT = 38.8$ meV ($T = 300$ K; the results vary slowly with incident energy in the thermal range, and taking a Boltzmann average makes no discernable difference). Previous applications of the FOM have employed elastic trajectories, as this allows the calculation of the probability that the incident atom will lose a given energy after traversing the adsorption well twice (i.e. in and out). The probability that this energy loss is greater than the incident energy of the atom gives a good estimate of the sticking probability, the quantity of interest in previous calculations. However, we are interested in all of the excitations that result from the atom relaxing into the adsorption well, hence we use a full inelastic trajectory to obtain the chemicurrent.

Results are shown for a range of Schottky barrier heights in Fig. 2, for H and D, and for both spin-constrained and spin-degenerate friction coefficients. In both cases the spin-constrained potential is used - the

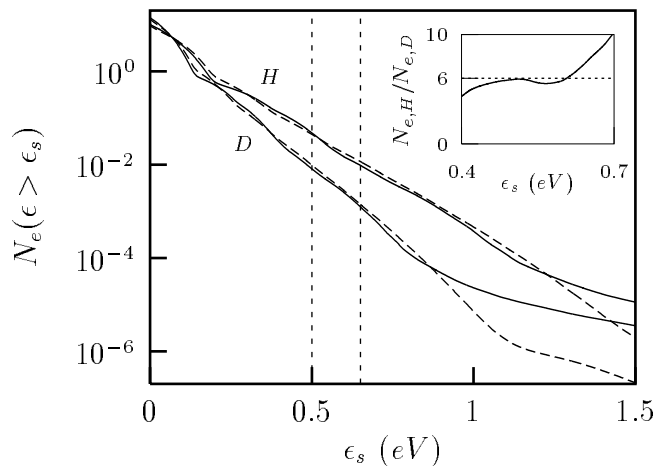


FIG. 2: Number of electrons per atom made available for detection over a Schottky barrier of height ϵ_s for H and D incident on the top site of Cu(111). Solid line is for friction resulting from constrained spin, and dashed line for spin-degenerate. The vertical lines span the range of Schottky barrier heights found by Nienhaus *et al.* for both Cu and Ag. Inset shows the ratio of the chemicurrents due to H and D, for constrained spin.

spin-degenerate calculation results in an unrealistically deep potential. Spin-degenerate chemicurrents differ from the spin-constrained case by $< 20\%$ for the barrier heights of interest. The similarity of the results for very different friction functions is a consequence of the incident atom spending a small proportion of the total trajectory in the region of space where the spin-degenerate and spin-constrained friction differ. If a large (though non-singular) friction is present around $z = 2.39 \text{ \AA}$ this will have little effect on the chemicurrent since the atom spends a short period of time and has a small velocity in this region (Eq. 3). We conclude that a precise description of friction in the region of the spin-phase transition is relatively unimportant, provided an unphysical singularity is avoided.

Before any comparison with experimental results may be made, detection efficiency must be estimated. As discussed by Nienhaus [7] two effects dominate the attenuation of electron current in their Schottky detectors. First we consider the loss of ballistic electrons due to scattering events in the thin metal film. This was found to be well described by an exponential decay, and for the device used to obtain the results above a ballistic mean free path (mfp) of 175 \AA was measured. For the film thickness of 75 \AA this results in attenuation by a factor of 0.65. Second, a transmission coefficient exists at the Cu/Si interface. This may be estimated from the results of Nienhaus [7] by comparison of the Cu/Si device with a multilayer device constructed by the deposition of a thin Cu film onto a Ag/Si detector, suggesting attenuation by a factor of $0.01 - 0.02$.

Correcting for these factors, and combining the uncertainties in the barrier heights and total attenuation factors, we may estimate a detected chemicurrent of $(0.63 - 1.90) \times 10^{-4}$ electrons/atom, which is in good agreement with experiment. We may also obtain a rough estimate of the chemicurrent for a Ag Schottky detector by using the experimentally measured Ag barrier height ($0.5\text{-}0.55 \text{ eV}$) in our Cu calculations. Correcting for an experimental mfp of 50 \AA [6, 7] (and Ag film thickness of 75 \AA) and using an estimated transmission of ~ 1 at the Ag/Si interface results in a chemicurrent of $(5.6 - 10.7) \times 10^{-3}$ electrons/atom for H. This again compares well with the experimental result of 4.5×10^{-3} electrons/atom [6].

An interesting signature of the experimental chemicurrent is the strong isotope dependence [6]. Our calculation predicts an unusually strong isotope effect due to the essentially exponential variation of the chemicurrent with barrier height, and simple energy scaling in the dynamics (we note that scaling the energy variable by $\sqrt{2}$ in $N_e(\epsilon > \epsilon_s)$ results in exact agreement between the chemicurrents for H and D for an elastic trajectory, and this holds approximately for the inelastic case). Nienhaus *et al.* reported no results for D incident on Cu, but for Ag the detected number of electrons/atom for H was larger

than for D by a factor of about 6. The inset in Fig. 2 shows the calculated ratio of chemicurrents for H and D, and in the range of relevant barrier heights we find an isotope effect close to the experimental result.

In summary, an *ab initio* description of the static adsorbate/metal surface and a dynamic FOM have been used to describe *e-h* pair creation. This approach includes energy loss by the classical incident atom consistently, and our results for H/Cu(111) are in good agreement with the chemicurrents measured by Nienhaus *et al.* Calculations show that simple dynamics can account for the large difference between the measured chemicurrents for H and D.

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